



A theoretical study on the equilibrium structures, vibrational frequencies and photoelectron spectroscopy of thiocarbonyl fluoride by using density functional and coupled-cluster theories



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ABSTRACT

The equilibrium geometries, vibrational frequencies and normal modes of F_2CS and F_2CS^+ \tilde{X}^2B_2 , \tilde{A}^2B_1 , and \tilde{B}^2A_1 states were obtained by utilizing both density functional and coupled-cluster (CC2) theories. Franck–Condon factors were calculated by using the harmonic-oscillator model taking into account the Duschinsky effect, based on which photoelectron spectra were simulated. The adiabatic ionization energies were computed by the CCSD(T) method extrapolated to the complete basis set limit. The computed equilibrium structures and vibrational frequencies are generally in agreement with the experiment, except in few cases. The B3LYP and CC2 approaches perform equally well in the computations of F_2CS . The simulated photoelectron spectra of F_2CS are also in accord with the experiment, indicating that the calculated structures are reliable. The computed adiabatic ionization energies are in agreement with the experiment within 0.01, 0.02, and 0.06 eV for the three ionic states, respectively.

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1. Introduction

The vibronic spectroscopy of molecules provides rich information about the equilibrium structures and vibrational energy levels of corresponding electronic states, which can be investigated theoretically by computing molecular properties together with Franck–Condon factors (FCFs) [1–20]. The FCF is the square of the Franck–Condon integral (FCI) which is defined as the integral of the product of vibrational wavefunctions of two electronic states [21–23]. In recent years, we have developed an analytical approach for computing FCIs of harmonic oscillators [24–29]. The Duschinsky effect [30] arising from mixing of vibrational normal coordinates between two electronic states of different equilibrium structures is explicitly treated in our approach. In the latest progress of our methodology, a general formula of FCI of harmonic oscillators with arbitrary dimensions has been derived and applied to study the photoelectron spectrum of ovalene ($C_{32}H_{14}$), a molecule possessing 132 normal modes [29]. Our approach is alternative to other relevant techniques (e.g., [1–20]) and the mature of FCI algorithms has made the theoretical studies of vibronic spectra of molecules convenient and compatible to experiments.

The experimental techniques of molecular photoelectron spectroscopy have been well developed since the 1970s [31,32].

However, theoretical methods capable of computing FCFs of polyatomic molecules were rare when a large number of molecular photoelectron spectra had been recorded. As a consequence, the experimental photoelectron spectra reported in that time were usually assigned according to empirical principles in conjunction with some theoretical computations of orbital energies. It might happen that the assignments were incorrectly made due to the lack of theoretical predictions about spectral patterns. For example, the first peak in the photoelectron spectrum of $H_2O^+(\tilde{B}^2B_2)$ state was assigned to the adiabatic transition by experimentalists, but Chang's computation indicated that it should correspond to the (0, 2, 0) vibrational state [26]. Similar inconsistency was also found for $D_2O^+(\tilde{B}^2B_2)$ where the first peak was better interpreted as the transition to the (0, 4, 0) vibrational state [26]. Accordingly, we claim that a reliable assignment of experimental vibronic (including photoelectron) spectra should be in harmony with FCF computations, provided that the model for calculating FCFs is adequate. On the other hand, the observed vibronic spectrum serves as a means to evaluate whether the computed equilibrium structures of excited (or ionic) states are in accord with experimental evidence, since the spectral patterns depend largely on the geometrical differences between the ground and excited (or ionic) states.

In this article, we present a theoretical study on the equilibrium structures, vibrational frequencies and photoelectron spectroscopy of thiocarbonyl fluoride (F_2CS). This compound was first prepared and isolated in 1962 by Downs who was also the first to identify

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all of its fundamental vibrations by recording the infrared spectra [33,34]. In 1965, Middleton et al. prepared F_2CS by the pyrolysis of its dimer, $(CSF_2)_2$ [35]. Later, Moule and Subramaniam carried out normal coordinate analyses for the five in-plane vibrational modes of F_2CS [36]. Hopper et al. measured the absolute intensities of infrared bands and obtained the normal coordinates of all six vibrational modes of F_2CS [37]. Hass et al. reported the gas phase and matrix infrared spectra as well as liquid phase Raman spectra of F_2CS around 1976 [38,39]. High resolution Fourier transform infrared spectra of F_2CS were reported and analyzed by Bürger and Jerzembek [40] in 1998 and by Flaoud et al. [41] in 1999. On the other hand, the microwave spectrum of F_2CS was first reported by Careless et al. in 1973 [42]. They also determined the equilibrium structure of F_2CS , in which the bond length $R_{CS} = 158.9$ pm, $R_{CF} = 131.5$ pm, and the bending angle $A_{FCF} = 107.1^\circ$ [42]. In 1992, Xu et al. recorded the Raman spectrum of F_2CS with a pulsed molecular-beam microwave Fourier transform spectrometer and reported the structure as $R_{CS} = 158.70$ pm, $R_{CF} = 131.82$ pm and $A_{FCF} = 106.89^\circ$ [43].

The electronic absorption spectra of F_2CS were investigated by Moule and co-workers in the 1970s for the singlet–singlet $\pi^* \leftarrow n$, $\pi^* \leftarrow \pi$ and singlet–triplet $\pi^* \leftarrow n$ transitions [44–46]. It was found that the structures in the corresponding excited states are nonplanar and the potential has double wells along the coordinate of the out-of-plane bending mode (ν_4). Recently in 2009, Zeng et al. discovered that matrix isolated F_2CS can photoisomerize to form cis- and trans-FCSF [47]. They also performed theoretical calculations to identify the possible pathways of photoisomerization. Earlier theoretical studies of F_2CS can be found in [48–54].

The photoelectron spectrum of F_2CS was reported by Kroto and Suffolk [55] in 1972 and by Mines et al. [56] in 1973. However, no theoretical studies on the structures of experimental spectrum were available since their publications, which was the motivation of the present study. In the experimental spectrum, some ionic states show clear vibrational structures. It is interesting that both $F_2CS^+(X)$ and $F_2CS^+(B)$ states have a hot band in their spectrum, whereas no hot bands are observed in $F_2CS^+(A)$ [55,56]. An accurate computation of FCFs should be able to account for the vibrational structures observed in different ionic states of F_2CS^+ , including the temperature effect which is crucial for hot bands. In addition, the relative intensities of hot bands in comparison to that of the origin band provide clues to determine the vibrational temperature of the experimental sample.

In this work, we computed the equilibrium geometries and vibrational frequencies of F_2CS and three lowest-lying ionic states of F_2CS^+ with density functional theories (DFT) and the second-order approximate coupled-cluster (CC2) theories. The results of time-independent and time-dependent DFT as well as the CC2 computations are compared with each other. The photoelectron spectra of F_2CS were simulated by computing FCFs with the approach developed in this group. We will show that both the simulated photoelectron spectra and the computed adiabatic ionization energies of F_2CS are in agreement with the experiment, indicating that the computed equilibrium geometries are reliable.

2. Computational methods

The equilibrium geometries, harmonic vibrational frequencies and normal modes of F_2CS and the three lowest-lying electronic states of F_2CS^+ were obtained by using the DFT approach with the B3LYP, B3PW91, and M06 functionals in conjunction with various basis sets up to aug-cc-pVTZ. The three ionic states studied are of different symmetry species in the C_{2v} point group, and thus can be optimized by using the time-independent DFT since each is the lowest one in energy among the states with the same symmetry.

However, the time-dependent DFT [57,58] of B3LYP and M06 were also applied to calculate the excited states of F_2CS^+ in order to compare the results with those obtained by time-independent DFT. In the time-dependent DFT computations, the geometries were first obtained by using symmetry constraints (C_{2v} point group). Then, the optimization was redone without symmetry constraints (C_1 point group) starting from a structure slightly distorted from the symmetric one. It was found that both the $F_2CS^+ \bar{A}$ and \bar{B} states converged to the C_{2v} structures as predicted by symmetry constraints. Besides, the CC2 computation employing the resolution-of-identity approximation [59–61] was performed under the C_1 point group and its results were consistent with those obtained by DFT. In other words, the present study shows that all the ionic states investigated belong to the C_{2v} point group.

With the data of equilibrium geometries, vibrational frequencies, and normal modes as inputs, the FCFs were computed by using the approach developed in this group in which the harmonic-oscillator model including the Duschinsky effect was coded [29]. Then, the photoelectron spectrum was simulated by summing the contributions from possible transitions in which FCFs were taken as the peak heights and the Gaussian function as the line shape. The adiabatic ionization energies (AIEs) were obtained by utilizing the CCSD(T) energies extrapolated to the complete basis set (CBS) limit [62] with aug-cc-pVXZ (X = D, T, Q, 5), in which the equilibrium geometries and zero-point energy (ZPE) corrections were taken from the B3LYP/aug-cc-pVTZ computation. While the DFT and CCSD(T) computations were performed by means of the Gaussian 09 package [63], the CC2 calculations were executed by the Turbomole programs [64].

3. Results and discussion

3.1. Equilibrium structures

Table 1 lists the optimized geometries of the ground state of $F_2CS(\bar{X}^1A_1)$ and the ionic states of $F_2CS^+(\bar{X}^2B_2, \bar{A}^2B_1$ and $\bar{B}^2A_1)$. As mentioned previously, all of the states studied belong to the C_{2v} point group. For F_2CS , our calculations are generally in agreement

Table 1
Calculated and experimental equilibrium structures of F_2CS and F_2CS^+ .

Method ^a	$F_2CS(\bar{X}^1A_1)$			$F_2CS^+(\bar{X}^2B_2)$		
	R_{CS}	R_{CF}	A_{FCF}	R_{CS}	R_{CF}	A_{FCF}
B3LYP/6-311+G(3df)	159.45	131.40	107.2°	166.54	126.23	115.5°
B3LYP/AVTZ	159.84	131.67	107.2°	167.09	126.48	115.6°
B3PW91/AVTZ	159.60	131.08	107.4°	166.67	126.06	115.8°
M06/AVTZ	159.71	130.00	107.5°	166.61	125.09	115.8°
MP2/6-311+G(3df) ^b	159.0	131.1	107.1°			
CBS-QB3 ^b	159.8	131.6	107.4°			
Experiment ^c	158.9	131.5	107.1°			
Experiment ^d	158.70	131.82	106.89°			
Method	$F_2CS^+(\bar{A}^2B_1)$			$F_2CS^+(\bar{B}^2A_1)$		
	R_{CS}	R_{CF}	A_{FCF}	R_{CS}	R_{CF}	A_{FCF}
B3LYP/6-311+G(3df)	173.56	125.27	114.0°	166.18	126.77	118.4°
B3LYP/AVTZ	174.15	125.53	114.1°	166.69	127.02	118.5°
B3PW91/AVTZ	173.45	125.16	114.2°	166.02	126.54	118.6°
M06/AVTZ	173.38	124.22	114.4°	166.11	125.20	118.8°
TD/B3LYP/AVTZ	173.90	125.59	114.2°	166.37	127.18	117.9°
TD/M06/AVTZ	173.71	124.13	114.6°	168.67	124.82	119.4°
CC2/AVTZ	173.52	125.49	114.2°	164.64	127.23	117.9°

^a AVTZ stands for aug-cc-pVTZ, R for bondlength (in pm), and A for bending angle.

^b Ref. [47].

^c Ref. [42].

^d Ref. [43].

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